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Title of Invention: Packing for an Automobile Exhaust Gas Purifier
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1. Scope of Patent Claims

The packing for an automobile exhaust gas purifier which is constructed by pasting together a vermiculite sheet and a ceramic fiber sheet and which is characterized whereby: (a) the above-mentioned vermiculite sheet is pressure molded into a sheet shape which possesses the required surface density in a mixture which is composed of (i) vermiculite particles which protrude in a layer and (ii) vermiculite particles with a diameter of over 35 mesh which do not protrude in a layer, with (i) and (ii) being mixed together in a ratio of 1 : 2 to 1 : 5 by weight, and an organic elastic bonding agent; and (b) the above-mentioned ceramic fiber sheet which is formed into a sheet shape by a bonding agent in which ceramic fibers, which are composed of alumina and silica and made with an average fiber length of over 50 mm and an average fiber diameter of 2 to 4 μm , are combined with natural rubber and polybutene.*

Detailed Explanation of the Invention

The present invention pertains to packing for an automobile exhaust gas purifier, and in particular pertains to the improvement of said packing which is composed of expanding sheet material that employs vermiculite as its raw material. Said expanding sheet material that employs vermiculite as its raw material (or packing which has been subjected to blanking or cutting) possesses excellent heat resistance against high temperatures, and

*[Translator: This word does not appear in any chemistry dictionary. It may be a misspelling for "polybutene"].

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moreover possesses a quality whereby it expands (referred to herein as "protrudes in a layer"*) due to heat, and based on this it has drawn attention as a packing material used as filler for machines which handle high temperatures, and the development of such uses has been undertaken. For example, in the case of an automobile exhaust gas purifier, which is constructed by housing a monolith-type catalyst body made of ceramic and of which the catalyst is made of precious metal supported on top of it inside a cylindrical container made of metal, the above-mentioned expanding sheet is used to fill the space between the monolith-type catalyst body (abbreviated below as "monolith") and the cylindrical container (abbreviated below as "outer cylinder") or as retentive material which supports the monolith.

Said monolith which has been used for the above-mentioned automobile exhaust gas purifier is composed of a ceramic foundation which possesses a low thermal expansion rate of approximately 1.2×10^{-6} /degrees Centigrade so that the three criteria for thermal resistance, heat resistant impact and a multi-contact surface area are respectively satisfied, and an extrusion molded item with a honeycomb wall of approximately 0.15 mm to 0.3 mm has been determined to be optimal for this. However, the difficult technical point in this purifier, as a whole, is the fact that there is a large difference between the monolith and the outer cylinder in the thermal and contraction rates. Therefore, special effort is required in order to retain the monolith inside the cylinder. In particular, examples in which exhaust gas purifiers are used near a higher temperature portion in the vicinity of the engine exhaust manifold have increased as a recent trend, and in such cases heat resistant steel whose thermal expansion coefficient is 1.5 times that of cast steel is employed for the material of the outer cylinder. In order to achieve an improvement in the performance for the three above-mentioned criteria, and when employing a monolith with a weak intensity and which has a thin honeycomb wall, the demand has arisen for packing which is more pliant than previous types and which has better cushioning properties. And for the purpose of further improvement to the performance of the monolith, there is also a demand for a gas seal whereby unpurified exhaust gas does not bypass the space between the outer cylinder.

Items possessing a variety of materials and structures have been proposed as retentive material for a monolith which can fulfill partially or almost completely the above-mentioned criteria. As one of these, an item which retains the monolith flexibly with a spring or bellows made of heat resistant steel and which has been compression molded by making thin metal wire into a latch net has been partially put into practical use as a flexible retentive material, but there are drawbacks to said material in that owing to abnormalities of the exhaust gas, etc., the temperature of the supported body overheats

*[Translator: This Japanese word appears to be a neologism coined expressly for this patent. Since I could not find it in any dictionary I have employed the above circumlocution to translate it.]

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and reaches over 600 degrees Centigrade, at which point the flexibility of the metal of the spring or bellows is lost and the material can no longer act as a retentive agent. In addition, in such a case, the monolith shakes and is finally destroyed due to the pressure of the exhaust gas and the vibration of the engine, etc. In addition, there is the further drawback that a molded item made with thin wire is too crude for sealing the exhaust gas, so complete purification cannot be achieved.

In addition, a method whereby an inorganic fiber material which possesses thermal resistance is filled into the space between the monolith and the outer cylinder has been proposed as a means which does not employ metal materials, and although said material is considered to possess the advantages that its thermally resistant temperature is high and that untreated exhaust gas does not leak after the crevice between the monolith and the outer cylinder is completely sealed, it is nonetheless necessary to make the fill density of the packing sufficiently high in order to retain the monolith effectively over a long period of time under conditions of vibration to the engine during operation and due to the heating and cooling cycle of the engine. Moreover, there is the drawback that the purification device becomes quite complicated in that a special outer cylinder, for example a multiple division-type metal cylindrical container, is used for the packing filler, a thick mat-shaped fiber material with the monolith wrapped inside it is forcefully compressed, and is fixed with a screw band, etc.

A method which improves the retaining of the monolith by using packing which grinds vermiculite particles into the inorganic fiber material, filling this into the space between the monolith and the container and forcefully compressing the inorganic fiber material after the vermiculite has protruded in a layer due to the exhaust heat of the engine has been proposed and has been partially put into practical use. However, even in the event that said packing with vermiculite ground into it is actually used for filling, under the current rigorous conditions for engines, it is necessary to fill, after forceful compression of the vermiculite, up to approximately 50 – 60% of the packing thickness in order to retain the monolith securely, due to the fact that accidents frequently occur in which the side walls of the monolith are damaged by the strong pressure which is applied.

In addition, as previously mentioned, for the present invention, when a sheet was constructed whereby vermiculite particles protruded in a layer due to heat, and to which ceramic paper, etc. was then pasted was proposed, even though such packing material exhibited excellent endurance of retentive force, the downfall was that there were complications from the standpoint of the processes used in winding the filler around the monolith and inserting the former into the latter because in order to determine the filler amount it was necessary to measure the dimensions of the outer diameter of the monolith, whose materials were hard and for which the dimensional tolerance was great.

After an investigation of the strengths and weaknesses of each kind of above-described packing, the inventors for the present patent have proposed said invention for the purpose of developing a packing which (a) the retentive properties of the vermiculite sheet

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material are fully realized; (b) is soft enough to easily insert into the narrow crevice between the above-mentioned monolith, whose dimensional tolerance is large, and the outer cylinder, which holds the former item in place; and moreover (c) the retentive force can hold up over a long time even under the changes due to the repetition of thermal expansion of the crevice's dimensions owing to the heating-cooling cycle between the high temperatures which occur at the time of exhaust gas purification and the ordinary temperatures when the engine is stopped.

Moreover, the impetus which led to the creation of the present invention was that said inventors noticed the fact that the vermiculite particle sheet and the sheets made of ceramic fiber, etc., which they had proposed, could be made separately. Said inventors also studied the method for manufacturing a sheet with vermiculite ground into it, in particular, vermiculite whose large particles were such that it was not possible to grind them uniformly based on the grinding technique. In addition, said inventors conducted repetitive testing and recognized the fact that there were changes in the retentive force [of many ceramic fibers] after long-term testing even when the retentive force in the initial period of the test was approximately the same as when they repeatedly carried out endurance tests for many ceramic fibers near actual use conditions. Said inventors discovered that only items within a certain range exhibited excellent performance; and that it was possible to provide a flexible sheet with refraction endurance which could adequately match the [characteristics of] an insertion device using a combination of natural rubber and polybutene as the flexible bonding agent for the ceramic fiber layer. It was this knowledge that contributed to the completion of the present invention.

As for the vermiculite (*hiruishi* in Japanese) used in said invention, it is a type of mineral mica, and it is known that when heated it takes on a book shape or an accordion shape due to its protrusion in a layer whose thickness is several hundred times greater than that when it is an ore owing to a process whereby the water between the layers which is contained in large quantities is caused to evaporate, and it is thereby possible to obtain a bulky particle shaped substance which is rich in acoustic absorption and thermal insulation properties. When mixed with various organic or inorganic bonding agents said substance is used in large quantities for building material and fire resistant material. In addition, plate-shaped bodies, such as steel plates which have been caused to protrude in a layer by heating after vermiculite ore has been filled into their crevices have very good cushioning properties and the fact that they can be employed as the retentive material of the monolith of an automobile exhaust gas purifier is the main point for the proposed invention. Said vermiculites are currently mined in Parabola, South Africa and Montana, North America and depending upon the application, can be used in a variety of particle diameters and degrees of protrusion in layers. The properties of said vermiculite particles are shown in Table 1.

| South Africa: Parabola product | North America: Montana product |
|--------------------------------|--------------------------------|
| Number 4: 3 – 7 mesh | #1: 3-10 mesh |
| Number 3: 5 – 12 mesh | #2: 8-14 mesh |
| Number 2: 9 – 24 mesh | #3: 10 – 35 mesh |
| Number 1: 16 – 42 mesh | #4: 25 – 65 mesh |

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In addition, the ceramic fibers which are employed in the present invention are made into thin fibers by fusing the ore, which combines alumina and silica in a ratio by weight of approximately 1[:1] and by using a high speed air stream or a high speed rotating disc. Regarding said ceramic fibers, the compounding ratio of $\text{Al}_2\text{O}_3 - \text{SiO}_2$ is changed according to the objective heat resistant temperature so that ceramic fibers are produced in the form of bulk-shaped aggregate bodies with fiber lengths of 25 to 250 mm and fiber diameters of 1.5 to 6 μm due to the difference between the temperature and the fiber formation formula of the molten liquid, and are then used in the form of paper blankets and textile products, etc. as heat insulating material used in high temperature applications that require a glass softening temperature of approximately 850 degrees Centigrade and a usage temperature of 1100 – 1500 degrees Centigrade.

The packing used for retaining a monolith-type catalyst based on the present invention is basically a sheet in which a mixture composed of a vermiculite sheet, namely vermiculite particles which have not protruded in a layer (as proposed by said inventors), vermiculite particles which are protruding in a layer and an organic flexible bonding material are pressure molded to a thickness of approximately 0.5 – 1.5 mm. In particular, vermiculite with fixed particle diameters are selected for a sheet onto which one or both sides is pasted an extremely flexible sheet composed of ceramic fibers and a special bonding agent. Due to the above-mentioned composition, an improvement is proposed whereby even under rigorous use, the retentive force is not lost.

The main point of the present invention concerns the packing for an automobile exhaust gas purifier which is characterized by the fact that in a packing for an automobile exhaust gas purifier which is composed by pasting together a vermiculite sheet and a ceramic fiber sheet, (a) the above-mentioned vermiculite sheet is pressure molded into a sheet shape which possesses the required surface density in a mixture composed of (i) vermiculite particles which protrude in a layer and (ii) vermiculite particles with a diameter of over 35 mesh which do not protrude in a layer, with (i) and (ii) being mixed together in a ratio of 1 : 2 to 1 : 5 by weight, and an organic elastic bonding agent; and (b) the above-mentioned ceramic fiber sheet which is formed into a sheet shape by a bonding agent in which ceramic fibers, which are composed of alumina and silica and made with an average fiber length of over 50 mm and an average fiber diameter of 2 to 4 μm , are combined with natural rubber and polybutene

The contents of the present invention will be explained in detail based on the embodiment below.

The application of the automobile exhaust gas purifier in which the packing described in the present invention is installed constitutes a monolith with an outer diameter of 94.5 ± 1.5 mm, a maximum monolith side wall temperature of 600 to 850 degrees Centigrade, an inner diameter of 100 mm for the outer cylinder made of metal, and a maximum temperature of 300 to 350 degrees Centigrade, which undergoes approximately 5 G of acceleration due to the vibration of the engine as a representative example. Regarding the amount of packing which is filled into the crevice (2.0 to 3.5 mm) between the monolith and the outer cylinder there is a concern that the monolith will be destroyed by an amount

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whereby the surface pressure when the packing is compressed to a minimum crevice dimension of 2.0 mm becomes greater than the surface pressure endurance of the monolith's side walls, and since on the other hand, if the surface pressure is too small, the retentive force for the monolith will decrease. Therefore, it was decided to use a test thickness (surface density) of the packing by taking the case in which the surface of the packing which has been compressed to the smallest crevice dimension reaches the intensity which the side walls of the monolith can withstand to be the maximum permissible filler amount.

Said inventors examined the test machine and test methods which should satisfy the above-mentioned engine conditions, and then did the following: (a) they wrapped the packing (25 mm in width) used for the test monolith around a cylinder made of quartz glass with an outer diameter of 93 mm; (b) they inserted said monolith, wrapped with said packing inside a cylinder made of heat resistant steel with an inner diameter of 100 mm and a flesh thickness of 6 mm by means of an insertion jig shaped like a mixing bowl with no bottom and with a taper attached and employed it as the test body; (c) they placed a lid on said test body; (d) they set the ordinary load by adding a spindle to the outer cylinder made of heat resistant steel so that the grinding stress would be equivalent to the force (0.7 kg) with which the monolith is extruded by the exhaust gas and the force (4.2 kg) with which the monolith is estimated to undergo at the time of shaking of 10 G; (e) Regarding the heating and cooling, they first adjusted the amount of power supplied so that the temperature in the outer cylinder increased 350 degrees Centigrade more than the temperature in the quartz glass interior within 30 minutes; (f) they then adjusted the compressed air volume which blows from the interior of the quartz glass cylinder so that the temperature dropped to 50 degrees Centigrade after another 30 minutes; (g) they then repeated this heating and cooling as 1 cycle; (h) they recorded the frequency of heating-cooling cycles endured in which the reinit switch operated when a gap of 2 mm arose between the quartz glass cylinder and the outer cylinder made of heat resistant steel under a condition of 4.9 kg; and (i) they judged that a test substance which had endured 50 such heating-cooling cycles had passed the test. For said test, the thermal expansion coefficient of the quartz glass cylinder was $0.5 \times 10^{-6}/\text{degree Centigrade}$, which is smaller than that of the monolith, which is $1.0 \times 10^{-6}/\text{degree Centigrade}$, and the load which was applied was greater than that which is applied when an actual engine is used.

Then, in order to determine the maximum permissible filler amount after setting the pressure resistant intensity of the monolith at 25 kg/cm^2 , a compression test was carried out by making a ceramic fiber sheet and a vermiculite sheet with compound amounts as shown in Table 2 below in order to provide answers to questions such as, how small a volume of vermiculate would be sufficient in order for the monolith retentive force to meet the required test conditions and how much ceramic fiber which possesses cushioning properties could be combined with this. A combination with a surface pressure of approximately 25 kg/cm^2 for a thickness of 2.0 mm, which is the minimum dimension for the crevice between the monolith and the outer cylinder, was selected.

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Table 2

| Test substance | Surface density of the ceramic fiber sheet | Surface density of the vermiculite sheet | Compressive stress of the crevice, 2.0 mm |
|----------------|--|--|---|
| (a) | 1.75 kg/m ² | 1.0 kg/m ² | 20.3 kg/cm ² |
| (b) | 1.35 | 1.35 | 24.2 |
| (c) | 0.95 | 1.80 | 41.0 |

(Refer to the embodiment provided below for the combination of the ceramic fiber sheet and the vermiculite sheet.)

Based on the above-mentioned table, in the event that the surface density of the packing used for the monolith is approximately 2.7 kg/m², the combination in (b) is appropriate, while in the case of (a) the amount of the vermiculite is small and as a result the endurance of the monolith retentive force is inadequate, and in the case of (c) the side walls of the monolith were destroyed when the monolith was inserted into the outer cylinder since it is above the pressure resistant intensity. Therefore, [the substance] with a surface density of (b) will be subsequently used as the test sample.

Next, an endurance test was carried out for the vermiculite and ceramic fibers which constitute the chief component materials of the packing for the present invention. The vermiculites are the products mentioned in Table 1, while the ceramic fibers involve items in which fibers with different average fiber lengths and average fiber diameters have been made into a sheet. The surface density of the ceramic fiber sheets and the vermiculite sheets are as stated above, and the results of the endurance test based on repetition of heating and cooling as described above are shown in Table 3.

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Table 3

| | | South Africa: Parabola product | | North America: Montana product | | | Compa- rative example |
|-----------------|-------------------|-----------------------------------|--------------------------------|-----------------------------------|-----------------------|-----------------------|-----------------------------|
| Fiber length | Fiber diameter | Number 3 5 - 12 mesh | Number 1 16 - 42 mesh | #2 8 - 14 mesh | #3 10 - 35 mesh | #4 28 - 65 mesh | #4 28 - 65 mesh |
| 50 mm | 6 μ | X (14) | | Circle | X (39) | | |
| | 2.2 μ | Circle | X (9) | Circle | Circle | X (8) | X (32) |
| | 1.5 μ | X (27) | | X (45) | X (12) | | |
| 32 mm | 6 μ | X (4) | | X (15) | | | |
| | 2.2 μ | X (8) | | Circle | | | |
| | 1.5 μ | X (3) | | X (9) | | | |

Vermiculite sheet surface density: 1.35 kg/m²

Ceramic fiber surface density: 1.35 kg/m²

The numbers in the parentheses indicate the number of times the heating-cooling cycle was carried out.

The X symbol indicates those items in which a gap of 2 mm between the cylinder made of quartz glass and the outer cylinder occurred.

The circle symbol indicates those items in which no gap occurred after 50 repetitions of the heating-cooling cycle.

In general, as far as vermiculite is concerned, those items with a large particle diameter are effective, and in addition, it has been determined that as far as the length and diameter of the ceramic fibers are concerned, those items with a long fiber length and whose diameter is in the area of 2.2 mm are superior. In addition, if one compares the case in which fine particles of vermiculite are ground into ceramic fibers, which is the prior art (with the combination and the sheet surface pressure being equivalent), with the examples cited in the present invention, it can be seen as shown in the comparative example in Table 3 that the endurance of the retentive force is insufficient and said [prior art] cannot be used under the rigorous conditions for the packing used for the monolith.

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As noted above, the present invention is composed of a vermiculite layer and a ceramic fiber layer, and since it is anticipated that the unexpanded vermiculite will expand to form a flexible sheet which protrudes in layers and that has a thickness several hundred times that of the original thickness, it is predicted that the endurance of the retentive force will be different in the case where it has been installed by making it adhere to the side walls of the monolith, which are a high heat surface, and the case where the vermiculite layer lies in the middle of the side walls of the monolith and the inner wall of the outer cylinder. The results of an endurance test in which a pasted packing possessing both densities "ceramic fiber sheet X kg/m² + vermiculite sheet Y kg/m² + ceramic fiber sheet Z kg/m²" [measured] from the side walls of the monolith is prepared as shown in Table 4 below, and it was determined that there was retentive force endurance only for combinations (A) and (B) in the table--that is, only when the vermiculite layer is close to the side of the monolith.

Table 4

| | | | Fiber length and fiber diameter of the vermiculite particles | 50 mm 2.2 μ North America: Montana product #2 | 50 mm 2.2 μ North America: Montana product #3 |
|-----|------------------------|------------------------|---|---|---|
| | Monolith side | Outer cylinder side | | | |
| | X | Y | Z | | |
| (A) | 0 | 1.35 kg/m ² | 1.575 kg/m ² | Circle | Circle |
| (B) | 0.20 kg/m ² | 1.35 kg/m ² | 1.35 kg/m ² | Circle | Circle |
| (C) | 0.20 kg/m ² | 1.35 kg/m ² | 1.13 kg/m ² | X (8) | X (19) |
| (D) | 0.20 kg/m ² | 1.35 kg/m ² | 0.90 kg/m ² | X (27) | X (21) |

The numbers in the parentheses indicate the number of times the heating-cooling cycle was carried out.

The X symbol indicates those items in which a gap of 2 mm between the cylinder made of quartz glass and the outer cylinder occurred.

The circle symbol indicates those items in which no gap occurred after 50 repetitions of the heating-cooling cycle.

Next, an account will be given of the bonding agent of the ceramic fiber. For the packing employed in the present invention, as described previously it is necessary to make vermiculite with a surface density of approximately 1.35 kg/m² into a sheet, and since the ceramic fiber sheet which is pasted to this has a bulk specific gravity of 0.13 g/cm³ in the ceramic fiber blanket it is not possible to use it as a packing for a monolith because its

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thickness is approximately 10 mm and moreover its intensity is weak. In addition, since items which can be acquired as paper have a bulk specific gravity of 0.3 kg/cm^2 , a thickness of 4.5 mm and also have some intensity, when pasted to the above-mentioned vermiculite sheet the two of them together become approximately 6 mm, and when it is wound in the circumference of the monolith, expansion force is applied to the ceramic fiber paper which constitutes the outer layer, and a problem occurs in that either the adhesion with the vermiculate is stripped off or even in the event that it is not stripped off, wrinkles are created on the vermiculite layer. In order to resolve these problems, a variety of bonding agents, such as rubber adhesives like NBR, SBR, NR, etc., were considered, and ultimately it was discovered that the above-mentioned difficulties did not occur only when NR and polybutene (PB) were combined. In other words, items in which NR and PB were combined, as shown in Table 5 below, had a thin sheet thickness. Even for sheets made of ceramic fibers with the same surface density, a thin sheet can be made in which adhesion with the vermiculite was complete and that stretched easily without any cracking and even when the monolith was bent to a diameter of 93 mm. In particular, as shown in example (g) in Table 5, items for which the NR and PB have been increased by double have thin layers, a high surface density, possess sufficient intensity and have sheet flexibility. This kind of ceramic fiber sheet is something which did not exist previously.

Table 5

| | Bonding agent | | | | Thick- ness | Findings when bending the monolith circumference diameter |
|---|---------------|------|------|-----|----------------|---|
| | NBR | SBR | NR | PB | | |
| a | 7.5% | | | | 5.3 mm | Crevice occurred |
| b | | 7.5% | | | 6.9 mm | Same as above |
| c | | | 7.5% | | 4.5 mm | Separation of vermiculite layer and ceramic fiber layer |
| d | | | 5 | 2.5 | 4.3 mm | Same as above |
| e | | | 2.5 | 5 | 4.0 mm | Excellent |
| f | | | | 7.5 | 12.0 mm | Lacking overall strength |
| g | | | 5 | 10 | 3.5 mm | Excellent |

Based on the above test data the comprehensive results are exhibited in the form of the embodiment below.

Embodiment

0.6 kg of bulky ceramic fibers with an average fiber length of 50 mm and an average fiber diameter of 2.2μ were placed in a 100 liter beater used for experiments and were mashed for 5 minutes on the beater edge without any load being applied. After the non-

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fiber portion which settled on the bottom of the beater was removed, a 0.45 kg ceramic fiber bulb was obtained. 45 g of polybutene manufactured by Nihon Sekiyu [Japan Petroleum], Inc. (HV - 300, kinematic viscosity of 32000 below 100 degrees) and 22.5g of natural rubber made by Levertechs, Inc. (LCS Levertechs) was added to this, and after fixing this by adding a small amount of aluminazol and a sulfuric acid band, said ceramic fiber bulb was made into a sheet of 1 m X 0.33 m by a hand grinding machine. After this was pressed with a surface pressure of 10 kg/cm² and dried, a semi-moist powder in which the following ingredients were mixed together was sprinkled approximately 5 mm thick on top of this ceramic fiber sheet.

| | |
|--|--------------|
| Number 3 vermiculite particles which protrude in a layer (Nichiasu product number T/#5888).... | 0.1 kg |
| North America Montana product vermiculite particles #2... | 0.35 kg |
| NR (LCS Levertechs 60% solid portion)... | 0.012 kg |
| Water... | 0.070 liters |

This was then spread evenly with a roller, and then on top of this was placed a thin sheet with the same combination as the above-mentioned ceramic fiber sheet, which had a surface density of 0.2 kg/m², and the two surfaces of the combined sheet were clamped together by a metal net. After applying a surface pressure of 15 kg/cm² the sheets were joined by the rubber latex which had oozed out from the layer of vermiculite semi-moist powder, and said laminated sheet was then dried, made into the form of a tape by cutting it to a width of 25 mm, and employed as the packing for the monolith.

The above-mentioned packing was then wrapped in the outer circuit of a quartz glass cylinder with an outer diameter of 93 mm which was selected for the monolith, and this was made into a test body by inserting the monolith, which had the packing wrapped around it, inside a cylinder made of heat resistant steel with an inner diameter of 100 mm and a flesh thickness of 6 mm by means of an insertion jig shaped like a mixing bowl with no bottom and with a taper attached. A lid was then placed on said test body, and an ordinary load was set by adding a 4.9kg spindle to the outer cylinder made of heat resistant steel so that the grinding stress would be equivalent to the force (0.7 kg) with which the monolith is extruded by the exhaust gas and the force (4.2 kg) with which the monolith is estimated to undergo at the time of shaking of 10 G. Then, with respect to the heating-cooling cycle, the amount of power supplied was adjusted so that the temperature in the outer cylinder increased 350 degrees Centigrade more than the temperature in the quartz glass interior within 30 minutes, and the compressed air volume which blows from the interior of the quartz glass cylinder was adjusted so that the temperature dropped to 50 degrees Centigrade after another 30 minutes. The heating-cooling cycle was then taken to be 1 cycle. After 50 such cycles were repeated, there was no gap between the quartz glass cylinder and the outer cylinder, so the result was deemed successful. In addition, even when tests were carried out by placing a purifier to which a filling was provided in the form of packing in both the front and rear of the monolith in the automobile engine, and the engine was run at full rotation for 200 hours, the results were excellent, with no damage being found on the monolith and no indication of the monolith having slipped out of place.

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As described above, according to the present invention, the packing for an automobile exhaust gas purifier which is constructed by pasting together a vermiculite sheet and a ceramic fiber sheet, can be characterized as (a) the above-mentioned vermiculite sheet is pressure molded into a sheet shape which possesses the required surface density in a mixture which is composed of (i) vermiculite particles which protrude in a layer and (ii) vermiculite particles with a diameter of over 35 mesh which do not protrude in a layer, with (i) and (ii) being mixed together in a ratio of 1 : 2 to 1 : 5 by weight, and an organic elastic bonding agent; and (b) the above-mentioned ceramic fiber sheet which is formed into a sheet shape by a bonding agent in which ceramic fibers, which are composed of alumina and silica and made with an average fiber length of over 50 mm and an average fiber diameter of 2 to 4 μm , are combined with natural rubber and polybutene. Therefore, it is possible to easily insert [said substance] into the narrow crevice between the monolith and the outer cylinder of an automobile exhaust gas purifier, thus an appropriate monolith retentive force is maintained over a long period even where changes occur due to the repetition of thermal expansion of the crevice dimensions due to the heating-cooling cycle of a high temperature at the time of exhaust gas purification and an ordinary temperature when the engine is stopped. Therefore, for the present invention, it is possible to contribute greatly to an improvement in the endurance of the automobile gas exhaust purifier.

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㉖特許請求の範囲

1 パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パッキンにおいて、前記パーミキュライトシートは、重量比で1:2~1:5に混合される膨張されたパーミキュライト粒と粒径35メッシュ以上の未膨張パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつてシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長50mm以上、平均繊維径2~4μよりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されていることを特徴とする自動車排気ガス浄化器用パッキン。

発明の詳細な説明

この発明は、自動車排気ガス浄化器用パッキンに関するもので、とくにパーミキュライトを原料とする膨張性シート材から構成されるパッキンの改良に関するものである。パーミキュライトを主材とする膨張性シート材（あるいは打抜き、裁断

加工したパッキン）は、高温に対して優れた耐熱性があり、かつ熱によつて膨張（膨張と呼ばれる）する性質があることから、高温を扱う機器の充填用パッキン材として注目され、その用途開発が行われている。たとえば貴金属触媒を担持させたセラミック製のモノリス型触媒体を金属製筒形容器内に収容して構成される自動車排気ガス浄化器にあつては、前記膨張性シートはモノリス型触媒体（以後モノリスと略称する）と筒形容器（外筒と略称する）との間の充填用として、あるいはモノリスを支持する保持材として使用されている。

上記の自動車排気ガス浄化器に使われている前記モノリスは耐熱、耐熱衝撃、多接触表面積の3つの要求をそれぞれ満足させるように、1.2×10⁻⁶/℃程の低熱膨張率を持つセラミック素地からなり、ハニカム壁0.15mm~0.3mm程の押出し成形品が最適とされているが、この浄化器全体の技術的難点は、モノリスと外筒との間に大きな熱膨張収縮率差があつて、モノリスを外筒内に保持するのに特別な工夫を必要とすることである。特に

最近の傾向として、排気ガス浄化器をエンジン排気マニホールド近傍のより高温部で使用する例が増え、この場合前記外筒材質に熱膨張係数が鋳鋼の1.5倍ある耐熱鋼材を採用したり、前記3つの性能向上を図るため、ハニカム壁が薄くて強度の弱いモノリスの採用を考える場合には、従来にも増して柔らかく、かつクッション性に富むパッキンが要求され、更にモノリスの性能を向上する理由で、モノリスと外筒との間を未浄化排気ガスがバイパスしないようなガスシール性も厳しく要求されるようになってきた。

上記要求を一部あるいはほぼ完全に満すことのできるモノリス用保持材パッキンとして、種々の材質・構造を持つものが提案されており、その一つとして耐熱鋼製のスプリングやベローズで弾力的に保持したり、また同材質の金属細線をメリヤス編みにして圧縮成形したものが、弾力性ある保持材として一部実用化されているが、排気ガスの異状などで、しばしば担持体の温度が過熱して600℃以上の高温になると、スプリングがベローズ成形品は金属の弾力性が失われ、保持材の役目をはたさなくなり、さらに排気ガスの圧力やエンジン等の振動により、モノリスががたつき、最終的に破壊してしまう欠点がある。また前記細線成形品は、排気ガスをシールするには粗すぎて、完全な浄化が期待できない点にも欠点がある。

また、金属材料を使用しない手段としては、耐熱性のある無機質繊維材料をモノリスと外筒との間に充填する手段が提案されており、このものは耐熱温度が高く、またモノリスと外筒との隙間を完全にシールし、未処理排ガスが漏れないことなどが利点とされているが、モノリスをエンジンや走行時の振動や熱冷サイクル下で長期間にわたり有効に保持させるには、パッキンの充填密度を充分高くする必要がある、またパッキン充填に特別な外筒、例えば複数分割型の金属製筒型容器を用意し、モノリスを中にくるんだ厚いマット状繊維材料を強く圧縮し、ネジ・バンド等で固定するような複雑な浄化装置となる欠点がある。

上記手段の改良と考えられるものとして、無機質繊維材料にパーミキュライト粒を抄きこんだパッキンを使用し、これをモノリスと容器との間に充填し、エンジンの排気熱によつてパーミキュライトが膨張して無機質繊維材料を強く圧縮し、そ

れによつてモノリスを保持する手段が提案され、一部実用化されている。しかしながら、このパーミキュライト抄きこみパッキンを実際に充填使用する場合でも、各種条件が厳しくなった現時点では、苛酷な実車条件下で確実にモノリスを保持できる場合は、パッキン厚さの50~60%程度にまで強圧して充填しなければならず、その強圧作用でモノリス側壁を破損する事故がしばしば発生している。

また、さきに本発明は、パーミキュライト粒が熱により膨張する性質をそのまま利用し、パーミキュライト粒をシート化し、セラミックペーパーなどと張り合わせたシートを提案したが、このパッキンは優れた保持力耐久性を示す反面、材質が固く、寸法公差の大きいモノリスの外径寸法を測定して充填量を決め、巻装挿入する工程上の複雑さがある。

本発明者は、前述した各種パッキンの長所短所を検討し、本発明者が先に提案したパーミキュライトシート材が大きな保持力耐久性を発揮する特性を活かし、寸法公差の大きい前記モノリスとそれを保持する外筒との間の狭い隙間に容易に挿入できるほど柔らかく、かつ排気ガス浄化時の高温・エンジン停止時の常温間の熱冷サイクルによる隙間寸法熱膨張繰返し変化下にも長期間にわたって保持力が保てるパッキンを開発する目的でこの発明を提供したものである。

更に、この発明をなすに到つたきつかけは、本発明者が提案したパーミキュライト粒シートとセラミックファイバーなどのシートが別々に作成しうることに着目し、パーミキュライトを抄きこむシートの製造法では、抄造技術上均一に抄きこめないような大粒のパーミキュライトについても検討し、また多くのセラミックファイバーについて実際の使用状況に近い耐久性試験を繰返して行つたところ、試験初期の保持力は同程度でも長期試験後の保持力に変化が認められ、ある範囲にあるもののみが優れた性能を示すことを見出し、またセラミックファイバー層の弾性結合材として天然ゴムとポリブテンとの組合わせにより、実際の挿入装置に充分適合できる柔軟性・耐屈曲性を付与できることを見出し、その知見にもとづいて、この発明を完成したものである。

この発明において使用されるパーミキュライト

(ひる石)は雲母鉱物の一種で、加熱すると多量に含有する層間水を発散させる過程で原石時の厚さの数百倍以上に膨積してブツク状またはアコーディオン状となり、吸音断熱性に富む、嵩高な粒状物が得られることが知られており、これに有機または無機系の種々な結合材を混合したものは建材・耐火材などに多量に利用されている。また、パーミキュライト原石を鉄板などの隙間に充填して加熱膨積させた板状体はクッション性に富み、自動車用排気ガス浄化器モノリスの保持体として使用できることは、本発明者が先に提案したとおりである。これらのパーミキュライトは、現在南ア・パラボラ産あるいは北米モンタナ産が入手でき、用途に応じて種々の粒径・膨積程度のものが利用されている。これらパーミキュライト粒の性状を表1に示す。

表 1

| 南ア パラボラ産 | 北米 モンタナ産 |
|--------------|--------------|
| 4号 3~7メツシュ | #1 3~10メツシュ |
| 3号 5~12メツシュ | #2 8~14メツシュ |
| 2号 9~24メツシュ | #3 10~35メツシュ |
| 1号 16~42メツシュ | #4 28~65メツシュ |

また、この本発明で使用するセラミックファイバーはアルミナとシリカの重量比がほぼ1の配合原料を電弧炉によつて熔融し、高速気流を利用して、あるいは高速回転円板を利用して細繊維化したものである。これらセラミックファイバーは目的とされる耐熱温度により、 $Al_2O_3 \cdot SiO_2$ 配合比を変え、熔融液の温度・繊維化方式の違いにより、繊維長25~250mm繊維径1.5~6 μ のバルク状集合体として生産され、ガラス軟化温度約850℃、使用温度1100~1500℃の高温用断熱材としてペーパーブランケット・紡織品などの形態で利用されている。

この発明によるモノリス型触媒保持用パツキンは基本的には、本発明者が先に提案したパーミキュライトシート即ち未膨積のパーミキュライト粒と膨積させたパーミキュライト粒と有機弾性結合材とからなる混合物が0.5~1.5mm程の厚さに加圧成形されたシートであつて、とくにパーミキュライトに所定の粒径のものが選択され、そのシート

の片面もしくは両面にセラミックファイバーと特殊な結合剤とからなる柔軟性に富んだシートが張り付けられた構成に特徴があり、この構成により苛酷な使用条件下でも保持力を失なわないよう改良したものである。

この発明の要旨とするところは、パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パツキンにおいて、前記パーミキュライトシートは、重量比で1:2~1:5に混合される膨積されたパーミキュライト粒と粒径35メツシュ以上の未膨積パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつてシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長50mm以上、平均繊維径2~4 μ よりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されている自動車排気ガス浄化器用パツキンである。

次にこの発明の内容を、その実施試験に基いて詳細に説明する。

この発明のパツキンが装着される自動車排気ガス浄化器の使用状態は、モノリス外径94.5 \pm 1.5mm、モノリス側壁最高温度600~850℃、金属製外筒内径100mm、最高温度300~350℃で、エンジンの振動による加速度を5G程度受ける例が代表的な例である。モノリスと外筒とのあいだの隙間(2.0~3.5mm)に充填するパツキン量については、パツキンを最小間隙寸法2.0mmに圧縮した時の面圧がモノリス側壁の耐圧強度以上になる量では、モノリスを破壊するおそれがあり、逆に少い場合はモノリスの保持力が低下するので、最小隙間寸法に圧縮したパツキンの面圧がモノリス側壁耐圧強度になる場合を許容最大充填量としてパツキンの試験厚さ(面密度)を決定した。

前記の実車条件を満足させるべく、試験機器・試験方法を検討し、外径93mmの石英ガラス製円筒の外周に試験すべきモノリス用パツキン(25mm巾)を巻き、テーパのついた指針の底を抜いたような形状の挿入治具を介して内径100mm、肉厚6mmの耐熱鋼製円筒内にパツキンを巻いたモノリスを挿入して試験体とし、この試験体に蓋をして、モノリスが排気ガスに押出される力0.7kgとモノリスが10Gに加振される時に受けると推定される

力(4.2kg)に相当するずり応力がかかるように、耐熱鋼製外筒に錘を加えて常時載荷しておき、加熱冷却は石英ガラス内部より外筒の温度が30分で350℃に昇るように、供給電力量を調節し、続く30分で50℃まで下るように、石英ガラス筒内部より吹きつける圧縮空気量を調節し、この加熱冷却を1サイクルとして繰返して行い、4.9kgの載荷により、石英ガラス筒と耐熱鋼製外筒との間に2mmのずれが生じた時にリミットスイッチが働き、耐久した熱冷サイクルの回数を記録させ、熱冷サイクルを50回耐えた試料を合格とした。なお石英ガラス円筒の熱膨張係数は $0.5 \times 10^{-6}/^{\circ}\text{C}$ で、モノリスの $1.0 \times 10^{-6}/^{\circ}\text{C}$ より小さく、また載荷している荷重も大きく、実車より同等以上の厳しい条件とした。

そこで、モノリスの耐圧強度 $25\text{kg}/\text{cm}^2$ と設定して許容し得る最大の充填量を求めるため、モノリス保持力を要求試験条件に合わせるには、どれ程少量のパーミキュライトで足りるか、またクツシヨン性のあるセラミックファイバーをどれ程多量に組合わせることができるか、下記表2に示す配合量のセラミックファイバーシートおよびパーミキュライトシートを作成して圧縮試験を行い、モノリス・外筒隙間の最小寸法である厚さ2.0mmにおける面圧が $25\text{kg}/\text{cm}^2$ 付近の組合せを選定した。

表 2

| 試料 | セラミックファイバーシートの面密度 | パーミキュライトシートの面密度 | 隙間2.0mmの圧縮応力 |
|-----|----------------------------|---------------------------|-----------------------------|
| (イ) | $1.75\text{kg}/\text{m}^2$ | $1.0\text{kg}/\text{m}^2$ | $20.3\text{kg}/\text{cm}^2$ |
| (ロ) | 1.35 | 1.35 | 24.2 |
| (ハ) | 0.95 | 1.80 | 41.0 |

(セラミックファイバーシートおよびパーミキ

表

| 繊維長 繊維径 | | 南ア・パラボラ産 | | 北米モンタナ産 | | | 比較例 |
|------------|-----------|----------------|-----------------|----------------|-----------------|-----------------|-----------------|
| | | 3号 5~12mesh | 1号 16~42mesh | #2 8~14mesh | #3 10~35mesh | #4 28~65mesh | #4 28~65mesh |
| 50mm | 6 μ | × | | ◎ | × | | |
| | 2.2 μ | ◎ | × | ◎ | ◎ | × | × |

ュライトシートの配合は後記する実施例参照)

上記の表より、モノリス用パツキンの面密度が $2.7\text{kg}/\text{m}^2$ 程の場合は(ロ)の組合せが適当で、(イ)の場合はパーミキュライトシートの量が少なく、モノリス保持力耐久性が不足し、(ハ)の場合は耐圧強度以上でモノリスを外筒に挿入する時モノリス側壁が破壊されたので、以後(ロ)の面密度を持つものを供試体とした。

次にこの発明によるパツキンの主構成材料であるパーミキュライト粒およびセラミックファイバーについて、耐久試験を行つた。パーミキュライトは前記表1に掲げた名柄、セラミックファイバーは平均繊維長と平均繊維径の異なるファイバーをシート化したものである。セラミックファイバーのシートおよびパーミキュライトシートの面密度は前に述べたとおりで、前述した加熱冷却の繰返しによる耐久試験結果は表3のとおりである。

| 繊維長 繊維径 | | 南ア・バラボラ産 | | 北米モンタナ産 | | | 比較例 |
|------------|-----------|----------------|-----------------|----------------|-----------------|-----------------|-----------------|
| | | 3号 5~12mesh | 1号 16~42mesh | #2 8~14mesh | #3 10~35mesh | #4 28~65mesh | #4 28~65mesh |
| | 1.5 μ | × | | × | × | | |
| 32mm | 6 μ | × | | × | | | |
| | 2.2 μ | × | | ◎ | | | |
| | 1.5 μ | × | | × | | | |

パーミキュライトシート面密度 1.35kg/ m^2

セラミックファイバー // 1.35 //

括弧内の数字は加熱冷却サイクルの回数。

×印は、石英ガラス製円筒と外筒とのあいだに2mmのずれが生じたもの。

◎印は50回の加熱冷却サイクルでずれが生じなかったもの。

総じてパーミキュライトは粒径の大きなものが有効で、またセラミックファイバーの繊維長は長くて繊維径の2.2 μ 付近のものが優れていることが判明した。また、従来の技術であるパーミキュライト細粒をセラミックファイバーに抄きこんだ場合（配合、シート面密度同等で）をこの発明の例と対比すると、表3の比較例に示すように、保持力耐久性が不足し、苛酷なモノリス用パッキンの条件下では使用できないことが認められた。

* この発明は前記の如くパーミキュライト層とセラミックファイバー層とからなり、未膨張のパーミキュライトが膨張して弾性のある、元厚の数倍の膨張性シートとなることが期待されているため、高熱面であるモノリス側壁に密着して装着されている場合と、パーミキュライト層がモノリス側壁と外筒内壁との中間にある場合とで保持力の耐久性が異なると予想され、モノリス側壁側より「セラミックファイバーシートXkg/ m^2 +パーミキュライトシートYkg/ m^2 +セラミックファイバーシートZkg/ m^2 」の両密度をもつ張り合わせパッキンを下記表4のように作成して耐久試験を行った結果、表中(A)、(B)の組合わせ時のみ、即ちパーミキュライト層がモノリス側に近い時のみ保持力耐久性があることが判明した。

表

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| | 繊維長 // 径 パーミキュライト粒 | | | 50mm 2.2 μ 北米モンタナ産 #2 | 50mm 2.2 μ 北米モンタナ産 #3 |
|---|--------------------------|---------------|----------------|------------------------------------|------------------------------------|
| | モノリス側 X | 外筒側 Y | Z | | |
| A | 0 | 1.35kg/ m^2 | 1.575kg/ m^2 | ◎ | ◎ |
| B | 0.20kg/ m^2 | 1.35kg/ m^2 | 1.35kg/ m^2 | ◎ | ◎ |
| C | 0.45kg/ m^2 | 1.35kg/ m^2 | 1.13kg/ m^2 | × | × |
| D | 0.68kg/ m^2 | 1.35kg/ m^2 | 0.90kg/ m^2 | × | × |

括弧内の数字は加熱冷却サイクルの回数。

×印は、石英ガラス製円筒と外筒とのあいだに

2mmのずれが生じたもの。

◎印は50回の加熱冷却サイクルでずれが生じな

かつたもの。

次にセラミックファイバーの結合剤について述べる。この発明のバツキンにおいては、前述したように、面密度 $1.35\text{kg}/\text{m}^2$ 程のパーミキュライトをシート化する必要があり、これに張り合わされるセラミックファイバーシートは、普通のセラミックファイバーブランケットでは嵩比重が $0.13\text{g}/\text{cm}^3$ であるから、厚さとして 10mm 程で、かつ強度が弱く、モノリス用バツキンとして取扱いができない。またペーパーとして手に入れるものは嵩比重が $0.3\text{g}/\text{cm}^3$ であるから、厚さ 4.5mm で、強度もあるが、前記パーミキュライトシートと張り合わせると、両者合わせて 6mm 程になり、これをモノリス周囲に巻きつけると、外層であるセラミックファイバーペーパーに伸張力がかかり、パーミキュライト層の接着が剥れるか、剥れない場*

*合でもパーミキュライト層にしわが寄る難点が生じた。これらの点を解決するため、種々の結合剤例えばNBR、SBR、NR等のゴム系接着を検討したところ、結局、NRとポリブテン (PB) を組合わせた時のみ上記難点が生じないことを見出した。即ちNRとPBを下記表 5 のように組合わせたものは、同じ面密度のセラミックファイバーのシートでも、シート厚を薄くでき、モノリス径 93mm に屈曲した状態でもパーミキュライトシートとの接着も完全でシートとして伸び易く、またキレツも生じない。特に下記表 5 の例 g のように、NRとPBを倍量に増加したものは、層が薄く面密度が高く、かつ強度も充分あつて、シート柔軟性があり、また良く伸びる性状を示しており、このようなセラミックファイバーシートは、従来存在しなかつたものである。

表

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| | 結合剤 | | | | 厚さ | モノリス周径に曲げた時の所見 |
|---|------|------|------|-----|---------|---------------------------|
| | NBR | SBR | NR | PB | | |
| a | 7.5% | | | | 5.3mm | キレツ発生 |
| b | | 7.5% | | | 6.9 // | // |
| c | | | 7.5% | | 4.5 // | パーミキュライト層・セラミックファイバー層間で剥離 |
| d | | | 5 | 2.5 | 4.3 // | // |
| e | | | 2.5 | 5 | 4.0 // | 良好 |
| f | | | | 7.5 | 12.0 // | 総合力なし |
| g | | | 5 | 10 | 3.5 // | 良好 |

以上の実施試験データをもとに総合した結果を下記実施例として示す。

実施例

平均繊維長 50mm 、平均繊維径 2.2μ のバルク状セラミックファイバー 0.6kg を 100ℓ の試験用ビーターに入れてビーターエッジに荷重をかけずに5分間叩解し、ビーターの底に沈殿した未繊維分(ショット)を除いて、 0.45kg のセラミックファイバーバルブを得て、これに 45g の日本石油製ポリブテン (HV-300、動粘度 100°F 32000) とレパーテックス社製天然ゴム (LCSレパーテックス) 22.5g (どちらもエマルジョン) を入れ、アルミナゾル・硫酸バンドを少量入れて定着させ、このセ

ラミックファイバーバルブを $1\text{m} \times 0.33\text{m}$ の手抄き抄造機でシート化し、面圧 $10\text{kg}/\text{cm}^2$ で圧搾して乾燥し、このセラミックファイバーシートの上

に、

3号膨積パーミキュライト粒 (ニチアス製品番号T/#5888) $\dots 0.1\text{kg}$

北米モンタナ産パーミキュライト粒#2 $\dots 0.35\text{kg}$

NR(LCSレパーテックス60%固形分) $\dots 0.012\text{kg}$

水 $\dots 0.070\ell$

を混合した半湿潤粉末を約 5mm 厚に散布し、ローラーで均一に伸展し、その上に $0.2\text{kg}/\text{m}^2$ の面密

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度を持つ前記セラミックファイバーシートと同配合の薄シートをかぶせて組合わせたシート両面を金網ではさみ、面圧 $15\text{kg}/\text{cm}^2$ で加圧し、パーミキュライト半湿潤粉末層からにじみ出したゴムラテックスでシート間を接合し、この積層シートを乾燥させ、 25mm 巾に載断してテープ状とし、モノリス用パッキンとした。

前記パッキンをモノリスに見立てた外径 93mm の石英ガラス製円筒の外周に巻き、テープのついた揺針の底を抜いたような形状の挿入治具を介して内径 100mm 、肉厚 6mm の耐熱鋼製円筒内にパッキンを巻いたモノリスを挿入して試験体とし、この試験体に蓋をして、実際のモノリスが排気ガスに押出される力 0.7kg とモノリスが 10G に加振される時に受けると推定される力(4.2kg)に相当するずり応力がかかるように、耐熱鋼製外筒に錘 4.9kg を加えて常時載荷しておき、加熱冷却は石英ガラス内部より外筒の温度が 30分 で 350°C になるように、供給電力量を調節し、続く 30分 で 50°C まで下るように、石英ガラス筒内部より吹きつける圧縮空気量を調節し、この加熱冷却を1サイクルとし、 50 サイクル繰返して行つた後も、石英ガラス筒と外筒との間でずれがなく、合格であつた。また前記パッキンをモノリスに前後2テープで充填した浄化器を自動車エンジンに組みこみ、

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エンジンフル回転 200 時間の台上試験を行つても、モノリスに損傷が認められず、またモノリスがずれた跡も認められず良好であつた。

以上に述べたように、この発明によれば、パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パッキンにおいて、前記パーミキュライトシートは、重量比で $1:2\sim 1:5$ に混合される膨積させたパーミキュライト粒と粒径 35メツシユ 以上の未膨積パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長 50mm 以上、平均繊維径 $2\sim 4\mu$ よりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されているものであるから、自動車排気ガス浄化器のモノリスと外筒との隙間に挿入配置するパッキンとして、狭い隙間に容易に挿入させることができ排気ガス浄化時の高温・エンジン停止時の常温間の熱冷サイクルによる隙間寸法熱膨張繰返し変化にも長期間にわたつて適正なモノリス保持力が維持されるパッキンが得られるものであつて、それにより自動車排気ガス浄化器の耐久性向上に大きく寄与することができる。

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